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The goal of this project was to synthesize $\gamma$-TiAl using low temperature chemical processing techniques. Four different chemical processes based on the electropositive and reducing power of lithium were used to investigate their potential for the synthesis of the aluminides. The reactions conducted in polar solvents resulted in the formation of TiAl along with TiC as a secondary phase. Among the various polar solvents attempted, THF appears to be the most suitable solvent since the carbide phase was very much reduced. It also appears from these preliminary studies that subjecting the precursors to pre-treatment in $H_2$ makes them stable towards oxidation. Washing the preheated powders in water at this stage helps in minimizing and even elimination to a large extent impurity phases which may be related to lithium. The uses of inert solvents were found to be unsuitable due to the formation of insoluble adducts that lead to the generation of the formation of unknown phases in addition to TiC. The presence of TiC as an impurity is related to the coordination of TiCl with the solvent. The process offers promise and future efforts should be concentrated on removal of the solvent molecules coordinated to the metal groups so that single phase $\gamma$-TiAl can be synthesized. At the same time, it is possible that these TiAl-TiC composites may have some potential structural application.

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# LOW TEMPERATURE CHEMICAL ROUTES TO SYNTHESIS AND PROCESSING OF TITANIUM ALUMINIDE INTERMETALLICS

## FINAL REPORT
### (Grant # F49620-95-1-0088)

## SUBMITTED TO

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# 1. Introduction

Titanium aluminide belongs to the class of intermetallics, and alloys in this system are emerging as revolutionary high temperature materials that could very well change the shape of future-jet turbines and hypersonic aircraft[1-3]. The low density of the titanium aluminides based on $Ti_xAl$ (x = 1 or 3, 4.2 g/cm$^3$ for $Ti_3Al$ and 3.9 g/cm$^3$ for TiAl) make them particularly suitable for turbine blade, disk and automotive valve applications. In addition, they display attractive high temperature properties such as strength, stiffness, etc. which make them a desired class of materials to replace existing superalloys. The material is currently processed using conventional metallurgical melting, casting and ingot metallurgy processes, while several powder metallurgical approaches including rapid solidification and mechanical alloying techniques have been examined.

Conventional melt solidification approaches while being useful necessitate that extreme care be exercised particularly in the processing of the γ alloy compositions. This is largely because of the lower ductility limit of these alloys and their extreme sensitivity to both impurities and uncontrolled thermal gradients in processing. This has caused for processing of smaller than normal ingots and the need to cool the ingots with precise care to avoid thermally induced cracking. Furthermore, complications exist in controlling chemistries with great precision when melt synthesis requires both refractory metal additions and high concentrations of aluminum. The use of gas atomization (GA) and plasma rotating electrode process (PREP) on the other hand, offer the potential of improved composition control and homogeneity, and enhanced hot workability for these alloys[4-7].

While the use of rapid quenching and mechanical alloying techniques provide opportunities for improved alloys and microstructure, these process routes suffer from an innate lack of control over problems that exist in synthesizing reactive metal powders. Blended elemental powders on the 10 μm and larger size scale suffer from agglomeration, lack of adequate control over particle size and morphology, impurities due to tremendous oxygen affinity of these oxophilic elements, and opportunities for acquiring detrimental ceramic inclusions. These problems pose significant obstacles in the processing of high quality aluminide articles with the desired phase(s) and microstructure for high temperature application. Further, commercial use of melt synthesized prealloyed aluminide powders currently increases alloy cost by at least five times. Clearly, there is a need to identify and develop any alternative synthesis methods with potential for large scale production of low cost aluminides and aluminide composites. One such

path is the use of chemical techniques to synthesize these intermetallic compounds and modification of their surface structure to induce atmospheric stability and protection against the deleterious influence of oxygen.

Chemical processing of materials has gained considerable importance over the last two decades particularly, due to its impact in the processing of advanced ceramics. These techniques involve the use of solution chemistry to form precursors that possess initial structures very close to the ultimately desired material. Thus, simple subsequent heat treatment at lower temperatures are needed to obtain the desired material. A process that has demonstrated this, and that has gained considerable popularity over the years is the sol-gel process[8-13]. With the advent of the sol-gel process considerable interest was generated in the use of solution techniques to process nanostructured ultrafine particles. These include aqueous and non-aqueous precipitation, colloidal processes including the Pechini process, hydrothermal and microemulsion techniques. All these processes essentially involve the use of soluble precursors which undergo complexation by the intrinsic polymerization of the reacting species or by addition of polymerizing agents after the formation of the main desired product. The result is the formation of either a gel form, a powder or a finely dispersed stable suspension.

The use of soluble starting materials and the reactions being conducted in suitable solvent systems provide for extremely good mixing at the molecular level of the individual reacting species. As a result, the mobile solvated molecules travel reduced diffusion distances (< 1000Å) which lead to extremely good compositional control. Also, the use of metalorganic precursors result in the formation of high purity materials. Moreover, use of proper catalysts further helps in controlling the nucleation and growth mechanisms, thereby leading to materials with different morphologies, and in both amorphous or nanocrystalline forms. In addition, with alterations of the surface chemistry, and the extent of polymerization of the reacting species, the reaction kinetics can be controlled to yield thin films, whiskers or fibers. The resultant gels or ultrafine particles are extremely fine with specific surface areas in excess of 200 m$^2$/gm which make the particles very reactive leading to considerable reduction in sintering temperatures[14-16]. This is particularly attractive for intermetallics owing to the potential of superplastic behavior at low temperatures. The materials could therefore possess novel properties and open avenues for new applications. Thus, chemical routes offer considerable opportunities over the existing routes used for synthesizing the aluminides. Table 1 compares the potential benefits of powders synthesized using chemical routes as opposed to traditional and non traditional metallurgical routes.

While, chemical techniques have been explored to a great deal in the synthesis of oxides and to a certain extent the non oxides, there is a scarcity of work performed in the area of synthesis of intermetallics. Though, recognized as a potentially vital area for long range development of intermetallics, apart from reports on the use of plasma assisted chemical vapor deposition using inorganic titanium precursors and aluminum vapor, the entire area involving the implementation of low temperature solution chemical routes seems to be unexplored[17,18]. The present report presents the results of a short term research effort that was conducted to identify novel low temperature chemical approaches to synthesize aluminide powders. The main objective of such a short term study was that its successful execution would form the basis of a long term research plan. The long term research endeavor would focus on obtaining a fundamental understanding of the molecular processes involved in the formation of the aluminides. At the same time, it would provide the opportunity to implement a novel concept which involves the use of organic molecular capping ligands to stabilize the surfaces of the aluminide particles towards attack by atmospheric oxygen. Following the stabilization of the surfaces of the particles an in-situ colloidal approach could be used to obtain a stable particle dispersion. The stable dispersion could be shaped and fabricated into a 'green' preform that would be amenable for easy consolidation after removal of the unwanted carbon in a reducing atmosphere. Furthermore, the proposed approach also affords the flexibility of introduction of other alloying elements such as Nb, Mo, etc.

## 2.    Methodology of the present chemical approach

The present chemical approach is based on the electropositive nature of alkali metals and their strong ability to act as reducing agents. Hence, the reactions studied in the present work included reduction of the transition metal halides using alkali metal in the presence of a polar or non polar solvent. The reactions are conducted in the solvent phase leading to the formation of either a completely or partially reduced solid product of the parent metal, while the alkali metal remains in the solid precursor as an alkali halide. Subsequent heat treatment of the precursor either directly in argon or in a combination of hydrogen and argon atmosphere results in the formation of the intermetallic phase. The alkali halide product being volatile is removed during heat treatment. The schematic reaction involved in the process is indicated below:
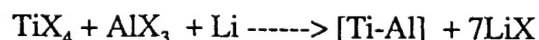
$$TiX_4 + AlX_3 + Li \longrightarrow [Ti\text{-}Al] + 7LiX$$
$$X = Cl, Br$$

The formation of the intermetallic is very strongly dependent on the ability of the alkali metal to attack titanium and aluminum halides and strip the metal salts of the halogen species, thereby

reducing them to the individual metals. However, transition metal halides are known to coordinate very strongly with polar organic solvents. This tendency to coordinate results in the formation of adducts which tend to be soluble. The nature of the adduct and the type of coordination exhibited by the transition metal with the polar end of the solvent molecule is very critical for the formation of the pure intermetallic. The process methodology that is described above is schematically displayed in Figure 1. In the present work, metal chlorides were used as the metal sources for conducting the reactions in polar organic solvents. However, due to the poor solubility of $AlCl_3$ in inert solvents, $AlBr_3$ was used as the metal source when employing benzene and hexane as the solvents for conducting the reaction. Four different solvent systems were used for conducting the reactions. The results of all these reactions are described in the subsequent sections.

## 3. Experimental Procedure

Materials Synthesis and Characterization

As mentioned above, four different processes were attempted to synthesize γ-TiAl. All the reactions were conducted in the absence of air and moisture. Titanium tetra-chloride ($TiCl_4$, Aldrich, 99.5%) was used as the metal source for titanium, while either aluminum tri-chloride ($AlCl_3$, Aldrich, 99.99%) or aluminum tri-bromide ($AlBr_3$, Aldrich, 99.99%) was used as aluminum source depending on the nature and type of solvents employed. Four processes were attempted using various polar and non-polar inert solvents such as acetonitrile, tetrahydrofuran, benzene and hexane. Figures 2-5 show a schematic of the procedures followed to synthesize the precursors for titanium aluminide. The details of each process are given below:

## A. Reactions conducted in polar organic solvents

Process I:

In the first process, aluminum tri-chloride was dissolved in anhydrous acetonitrile ($CH_3CN$, Aldrich, 99.5%) and stirred for about 10 min to dissolve $AlCl_3$ completely. Titanium tetra-chloride was then added to the solution with 1:1 molar ratio of $AlCl_3$ to $TiCl_4$, and mixed for 10 min. After obtaining a clear solution of $AlCl_3$ and $TiCl_4$ in acetonitrile, lithium foil corresponding to the stoichiometric amount was added to the solution in order to induce the reduction and precipitation reaction. After the lithium foil was entirely consumed, the vessel was sealed and the precipitate was allowed to settle at the bottom of the vessel. The clear liquid was then decanted to collect the precipitate. The collected precursors was dried under vacuum at ≈ 150°C and then the dried powder was further heat treated in various heat-treatment

conditions. Figure 2 is a schematic flow sheet showing the procedure followed for the synthesis of the precursors.

Process II:

Identical procedure was followed as in process I except that tetrahydrofuran (THF, $C_4H_8O$, Aldrich, 99.5%, anhydrous) was used as a solvent. A schematic of the procedure followed is shown in Figure 3.

## B.   Reactions conducted in inert solvents

Process III and Process IV:

In processes III and IV, $AlBr_3$ was used as the source for aluminum because of the poor solubility of $AlCl_3$ in inert solvents such as benzene ($C_6H_6$, Aldrich, 99.5%, anhydrous) and Hexane ($C_6H_{14}$, Aldrich, 99.5%, anhydrous). In these processes, an adduct was seen to form after adding $TiCl_4$ to the solution of $AlBr_3$ in benzene. This was visible by the distinct change in color (formation of a dark brown solid) that was observed after mixing the two halide salts. The precipitate adduct was then allowed to settle. The clear supernatant liquid containing the two halide salts was then taken to which was added stoichiometric amounts of Li metal in the form of strips. The solutions containing all the reagents were then stirred for a longer time (12 h) since the reaction was perceived to be very slow in comparison to processes I and II.

The precursors synthesized using the above four processes were immediately heat-treated following the schedule as shown in Table 2 to investigate the effect of heat treatment condition on the crystallization of titanium aluminide. In order to identify the presence of crystalline phases, X-ray diffraction was performed using a Rigaku $\theta/\theta$ diffractometer. No X-ray analysis was conducted on the precursors because of their extreme reactivity to air and moisture, and also because of the possible potential hazards that could result on exposure of the precursor to moisture. Finally, the powders obtained from the processes which showed the presence of TiAl were observed for their morphology and particle size using a CamScan scanning electron microscope.

## 4.   Results and Discussion

The objective of the research effort as mentioned earlier is to identify a chemical process for the synthesis of $\gamma$-TiAl powders. Four different processes were therefore attempted to investigate their potential for the formation of the intermetallic. The precursors obtained from all the four processes were therefore heat treated and analyzed for the presence of crystalline phases. The results of the characterization of the four different precursors are discussed below:

(i) Process I

The precursors obtained by conducting the reduction reaction in acetonitrile were subjected to direct heat treatment in argon to investigate the crystallization and formation of the intermetallic phase. These heat treatments were conducted at a temperature of 1200°C since low temperature heat treatments would only show the presence of crystalline LiCl. When these precursors obtained in acetonitrile solvent were directly heat-treated in Ar at 1200°C for 10 h, x-ray analysis showed the presence of only titanium carbide, TIC to be the major crystalline phase (see Fig. 6). The minor phase marked 'unknown' could be related to the presence of titanium hydride. The exact mechanism for the formation of the carbide phase is unknown however, a plausible explanation for its formation could be suggested. Since the starting materials do not have any primary carbon bonds in them, the origin of carbon could only be associated with the solvent phase. It is known that transition metals form coordination bonds with donor ligands. We have also shown in our earlier work that $MoCl_5$ tends to form a strong adduct with acetonitrile when reacted with it for an extended period of time[19]. Two types of adducts have been identified in the case of Mo. We have also shown that the η-coordinated bond is extremely robust and cannot be replaced in the presence of any strong nucleophiles. Heat treatment of these adducts therefore invariably result in the formation of some carbide phase as an impurity.

The formation of a similar bond between Ti and acetonitrile can therefore easily be envisaged. It should be noted however, that the η-coordination in Mo tends to occur only after prolonged reaction (24h). The formation of such a strong adduct in the case of Ti could be expected to be rather rapid since the solution of the halide in acetonitrile is reacted with lithium almost immediately after dissolution. In order to eliminate the presence of carbon in the precipitate, pre-treatment in $H_2$ was therefore attempted. The hydrogen heat treatment was conducted at 800°C. After heat treatment for 10 h, x-ray diffraction conducted on the heat-treated powder revealed lithium chloride to be the major phase accompanied by a small amount of titanium hydride, $TiH_{1.924}$, (see Fig. 7(a)). The peak at 2θ angle of 62.5 is however, unknown and could not be related to any known phase. The presence of lithium chloride as mentioned earlier can be expected because of its ability to extract chlorine from the corresponding metal chlorides. Its presence therefore confirms the mechanism of the reduction reaction briefly discussed earlier. Lithium chloride was totally removed by washing the precursors pre-treated in $H_2$ with water. X-ray analysis conducted on the water-washed precursors show only small peaks corresponding to titanium hydride (Fig. 7(b)). Both, the precursors pre-treated in $H_2$ as well as the precursors washed in water after $H_2$ treatment were

then heat-treated in Ar at 1200°C for 10 h to crystallize the titanium aluminide phase. X-ray analysis conducted on both precursors show the presence of a mixture of TiAl and TiC (refer to Fig. 7(c) and (d)), while the sample directly heat-treated in Ar at 1200°C for 10 h reveals only TiC. The pattern displayed in Figure 7(d) does not contain any of the unknown phases that are seen in Figure 7(c). This suggests that the unknown phases are probably related to some water soluble impurities perhaps containing lithium. More characterization studies are essential before any firm conclusions can be made. These results indicate that pre-treatment in $H_2$ at 800°C is beneficial for minimizing the carbon content of the precursors and facilitates the formation of crystalline $\gamma$-TiAl phase. However, it is also possible that the pre-treatments in $H_2$ does induce the formation of some unknown phases which could be related to Al and Ti-hydrides.

In order to remove more carbon from the precursors and with the consequent intention of eliminating it completely, the as-prepared precursors were pre-treated in $H_2$ for a longer time and at a lower temperature. Lower temperatures of 300°C-600°C were selected since the formation of methane is known to be thermodynamically favorable at these temperatures [20,21]. Accordingly, the as-prepared powders were heat-treated in $H_2$ at 300°C and 400°C for 24 h respectively, and at 600°C for 2h. After this heat-treatment, the precursors showed the formation of titanium hydride ($TiH_{1.924}$) and AlLi phases while the intensity of peaks corresponding to LiCl decreased (see Fig. 8(a)). Presence of AlLi and reduction in intensity of LiCl suggests that chlorine could be removed in the form of HCl during the long heat-treatment in $H_2$ conducted at lower temperatures. This obviously is not the case when the precursors are heat treated in $H_2$ at 800°C for 10 h. Fig. 8(b) shows the X-ray diffraction trace obtained on the precursors after heat-treatment in $H_2$ at 300°C, 400°C, and 600°C, followed by Ar treatment at 1200°C for 10 h. Despite the pre-treatments of the precursor in $H_2$ for an extended period of time, XRD analysis of the final product after Ar treatment still reveals the presence of TiC, and $\beta$-$AlH_3$ in addition to TiAl. At the same time, as shown in Figure 8(b), a number of unknown phases are also seen to form. The peak positions for these unknown phases are similar to those seen in the pattern displayed in Figure 7(c) suggesting the presence of some lithium containing impurities. The presence of TiC and the formation of hydride is an indication that $H_2$ treatment is not sufficient for removal of carbon which is necessary to obtain the single phase of TiAl. Figure 9 is an SEM micrograph of the powders obtained after pre-treating in $H_2$ at 800°C prior to subjecting them to Ar heat treatments. The micrograph shows the morphology of the heat-treated powders containing a mixture of TiAl and TiC. These powders by and large consist of agglomerates of TiAl and TiC and the size of each agglomerate is approximately 1.5 μm. It should be noted that the agglomerated nature of the clusters seen in the micrographs do not

indicate the exact size of the primary crystallites. Transmission electron microscopy would provide a better idea of the exact crystallite sizes. However, close observation of the micrograph reveals several particles which are clearly extremely fine and in the sub-micron range. It is difficult at this stage to know the phase identity of these fine crystallites due to the presence of the mixed phases.

Thus, it can be seen that the reduction reaction postulated earlier does occur leading to the formation of $\gamma$-TiAl. However, it appears that the strong interaction of the solvent and $TiCl_4$ leads to the generation of primary Ti-C bonds in the precursor. The presence of these linkages in the precursor facilitates the formation of the carbide in addition to the intermetallic phase. In an attempt to reduce and eliminate the carbide formation it was decided to conduct the reactions in polar organic solvents that are not open chain derivatives. Tetrahydrofuran (THF) was therefore selected as the solvent medium despite the presence of oxygen as the donor site in this solvent. It was anticipated that oxygen in THF has only a lone pair of electrons thereby resulting in a normal $\sigma$- coordination bond rather than the more robust side-on, $\eta$- coordination. The normal $\sigma$- coordinated THF-group can be easily replaced in the presence of strong nucleophiles as we have shown in our studies of formation of nitrides using $MoCl_5$.

(ii) Process II

Tetrahydrofuran (THF, $C_4H_8O$) was therefore used as a solvent for conducting identical reactions instead of acetonitrile. As mentioned, the oxygen bonded to hydrocarbons in THF has a partial negative charge, which will be coordinated to the positive metal centers thus minimizing the formation of metal-carbon bonds as in the case of acetonitrile. The precursors derived using THF solvent were directly heat-treated in Ar at 1200°C for 10 h similar to the case of acetonitrile. X-ray analysis in this case, still revealed a mixture of TiAl and TiC to be the major phases (see Fig.10) similar to the powders obtained after heat treatment of the precursors derived using acetonitrile. There are some unknown phases whose peak positions appear to be similar to those displayed in Figure 7(c). This once again suggests the close similarity of the mechanisms involved in this process to process I. However, there was a difference. In the case of precursors derived using acetonitrile, when they were directly heat treated in Ar at 1200°C, X-ray analysis revealed the presence of only single phase TiC (see Fig. 6). Thus, these powders indicate phases similar to the powders obtained after $H_2$ and Ar treatment of precursors derived using acetonitrile. Pre-treatment of the precursors in $H_2$ followed by a water washing step could eliminate these unknown phases and leave behind the composite mixture of TiC and $\gamma$-TiAl. These results indicate that the use of THF as a solvent does result in a reduction in the carbon content compared to the powders obtained by

conducting the reaction in acetonitrile. Titanium tetrachloride is known to form a 1:1 ($TiCl_4 \cdot C_4H_8O$) and 1:2 ($TiCl_4 \cdot 2C_4H_8O$) type of adducts with THF. Most of these are known to decompose at temperatures of $\approx 140°C$[22]. However, the fact that carbide is seen in the present approach leads us to believe that stable adducts are formed which do not completely decompose. At the same time, there could also be opening of the ring by the presence of $AlCl_3$ in which case the formation of organolithium compounds and the subsequent formation of organotitanium compounds cannot be discounted. In any case, it therefore appears that the formation of TiC is linked to the generation of adducts due to the interaction between the metal chlorides and the solvent. In order to overcome this problem, it was decided to conduct the reaction in inert hydrocarbon solvents wherein no interaction between the solvent and metal halides can be foreseen. This formed the basis for processes III and IV. Accordingly, inert solvents possessing linear and aromatic ring structures were selected.

(iii) Process III

Benzene was used as a solvent of choice from the aromatic class due to its inert nonpolar nature. In this case, $AlBr_3$ was used as the source for aluminum because of the poor solubility of $AlCl_3$ in benzene. Titanium chloride, $TiCl_4$ was added to this solution of benzene after the dissolution of $AlBr_3$. The addition of $TiCl_4$ resulted in the formation of a brown-colored adduct in benzene. This adduct was very slightly soluble in benzene. In order to test the feasibility of the approach, the clear supernatant liquid was taken and Li metal strip was added to the solution. The reaction between the solution of the halides and Li metal was relatively slow however, precipitation occurred after stirring the solution for 12h. When this precursor was heat-treated in $H_2$ at 800°C for 10 h, X-ray diffraction revealed unknown phases, which may be related to some volatile lithium containing slats and hydrides of Ti and Al (see Fig. 11(a)). It is natural to expect this since the reaction was conducted using the supernatant liquid, whose stoichiometry was obviously very different from the starting composition. Subsequent heat treatment of this precursor in Ar at 1300°C for 10 h revealed the formation of single phase of TiC as shown by the X-ray analysis (refer to Fig. 11(b)). The formation of TiC in this case probably relates to the opening of the benzene ring by Li in the presence of $TiCl_4$ thereby leading to the formation of organotitanyl compounds. Subsequent pyrolysis in Ar therefore results in the formation of TiC as shown by our results. Thus, the inert nature of benzene is probably lost due to the combined presence of Li and $TiCl_4$. Another explanation could be that the combined presence of Li and $TiCl_4$ helps in polarizing the electrons in the aromatic ring of benzene facilitating the coordination of $TiCl_4$ with benzene. Subsequent heat treatment in Ar could help in consolidating the existing coordination further leading to the formation of TiC. In

fact, it has been reported that $TiCl_4$, aluminum and $AlCl_3$ react in benzene to form an arene-titanium (II) complex, $C_6H_6.TiCl_2.2AlCl_3$[23]. It is possible that the present process resulted in the formation of such a complex and the reaction with lithium facilitated the extraction of chlorine. Subsequent pyrolysis therefore resulted in the formation of TiC, while Al could have been lost during the $H_2$ pre-treatment as a volatile hydride. Since the above results indicated the adverse effect of using an inert aromatic solvent, it was decided to employ an inert linear chain saturated hydrocarbon as a solvent for conducting the reaction. This formed the basis of Process IV.

### (iv) Process IV

Hexane was selected as the inert solvent of choice in the linear straight chain saturated hydrocarbon category. In this case also $AlBr_3$ was used as the source for aluminum because of the poor solubility of $AlCl_3$ in hexane. Similar to the reaction in benzene, the addition of $TiCl_4$ to the solution of hexane containing $AlBr_3$ caused the formation of a brown solid adduct with $AlBr_3$. This adduct was also very slightly soluble in hexane similar to the reaction in benzene. The supernatant liquid was therefore taken for conducting the reaction to investigate the potential of the process for observing the formation of TiAl, if any. Hence, similar to process III, Li metal strip was added to the clear supernatant solution containing the metal halides. The reaction was extremely slow similar to process III and noticeable precipitation was observed only after stirring the solution for 12h. The precursors were then heat treated in Ar at 1300°C for 10 h similar to the treatment conducted on the precursors in process III. X-ray diffraction analysis conducted on the heat treated powders shows the formation of a mixture of TiAl, TiC and unknown phases (see Fig. 12). The close similarity in the peak positions of the phases marked 'unknown' to those seen in Figure 10 and Figure 7(c) suggests that they may be related to some lithium containing compounds which could be removed by washing the precursors in water after subjecting them to pre-treatment in $H_2$ similar to that conducted in process I. Thus, the use of hexane is perhaps better than benzene since the formation of some TiAl is evidently noticed. However, the formation of TiC is also seen as is the case with every process that has been studied in the current work. The mechanism for formation of TiC is once again not very clear in this case but, based on the results a plausible explanation could be provided.

Once again it could be postulated that $TiCl_4$ perhaps catalyzes the reaction of Li with hexane thereby forming an organolithium compound. The hexyl lithium compound could then react with $TiCl_4$ resulting in the formation of an organotitanyl compound. Pyrolysis of this compound can then lead to the formation of TiC. The fact that some TiAl is seen suggests that this is not the only reaction occurring. It is possible that the reduction reaction is also occurring

simultaneously while the organotitanyl compound is being generated. Thus, the formation of an organotitanium-aluminum compound could be a possible reason for the formation of the mixed TiAl and TiC phases in the final product.

## 5. Summary

Four different chemical processes based on the electropositive and reducing power of lithium were used to investigate their potential for the synthesis of $\gamma$-TiAl. Four different solvents belonging to the polar and inert category were also used for the current investigation. The reactions conducted in polar solvents resulted in the formation of the aluminide phase along with TiC as a secondary phase. In this category, THF appears to be the most suitable solvent since the carbide phase was very much reduced. It also appears from these preliminary studies that subjecting the precursors to pre-treatment in $H_2$ makes them stable towards oxidation. Washing the preheated powders in water at this stage helps in minimizing and even eliminating to a large extent impurity phases which may be related to lithium. The water washed precursors have by and large resulted in X-ray phase pure composites containing TiC and $\gamma$-TiAl. The use of inert solvents were found to be unsuitable due to the formation of insoluble adducts and the formation of unknown phases in addition to the formation of TiC. The results of this short term research project therefore do indicate the potential of the current approach for the formation of intermetallics in the Ti-Al system. The presence of TiC as an impurity phase should not undermine the true potential of this process. In fact, the process at the present state of research does represent a novel approach for the formation of in-situ composites containing TiAl and TiC. It may be possible that these composites may have some potential structural applications. The presence of TiC as an impurity is related to the coordination of $TiCl_4$ with the solvent. Future efforts should be concentrated on removal of the solvent molecules coordinated to the metal groups. Such efforts are currently underway and will be useful in demonstrating the applicability of these processes for the synthesis of the aluminides. The successful elimination of the carbide phase would certainly make this process unique in terms of synthesizing fine intermetallic powders. The approach can also be extended to the synthesis of a whole range of intermetallics containing several transition metals such as Nb, Mo, etc. Further characterization and optimization studies are clearly necessary to prove the strength of the process.

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**Table 1. Comparison of Existing methods and Chemical routes to process Titanium Aluminide Intermetallics**

| A. Melt solidification | B. Powder Metallurgy and Rapid Solidification Processes |
|---|---|
| - Not easy<br>- Thermally induced cracking<br>- Small components<br>- Long annealing treatments<br>- Solidification segregation<br>- Unmelted inclusions<br>- Ceramic inclusions | - Improved homogeneity<br>- Near Net Shape<br>- costly<br>- impurities (especially oxygen and inclusions)<br>- need for thermomechanical process<br>- coarse, agglomerated powders |

**C. Chemical Routes**

- high purity
- goodmolecular mixing and control of stoichiometry
- ultrafine particles
- control of particle shape, morphology and structure
- versatility of obtaining powders, films and fibers
- control of particle morphology to facilitate low temperature sintering

**Table 2.** **Heat treatment schedule for heat treatment of various precursors**

|   | Solvent | Temperature of preheat-treatment in $H_2$ (°C) | Temperature of heat-treatment in Ar (°C) |
|---|---|---|---|
| 1 | MeCN | N | 1200°C (10h) |
| 2 | MeCN | 800°C (10h) | 1200°C (10h) |
| 3 | MeCN | 300°C (24h), 400°C (24h) and 600°C (2h) | 1200°C (10h) |
| 4 | THF | N | 1200°C (10h) |
| 5 | Benzene | 800°C (10h) | 1300°C (10h) |
| 6 | Hexane | N | 1300°C (10h) |

N : not conducted

**Figure 1. Methodology of the process**
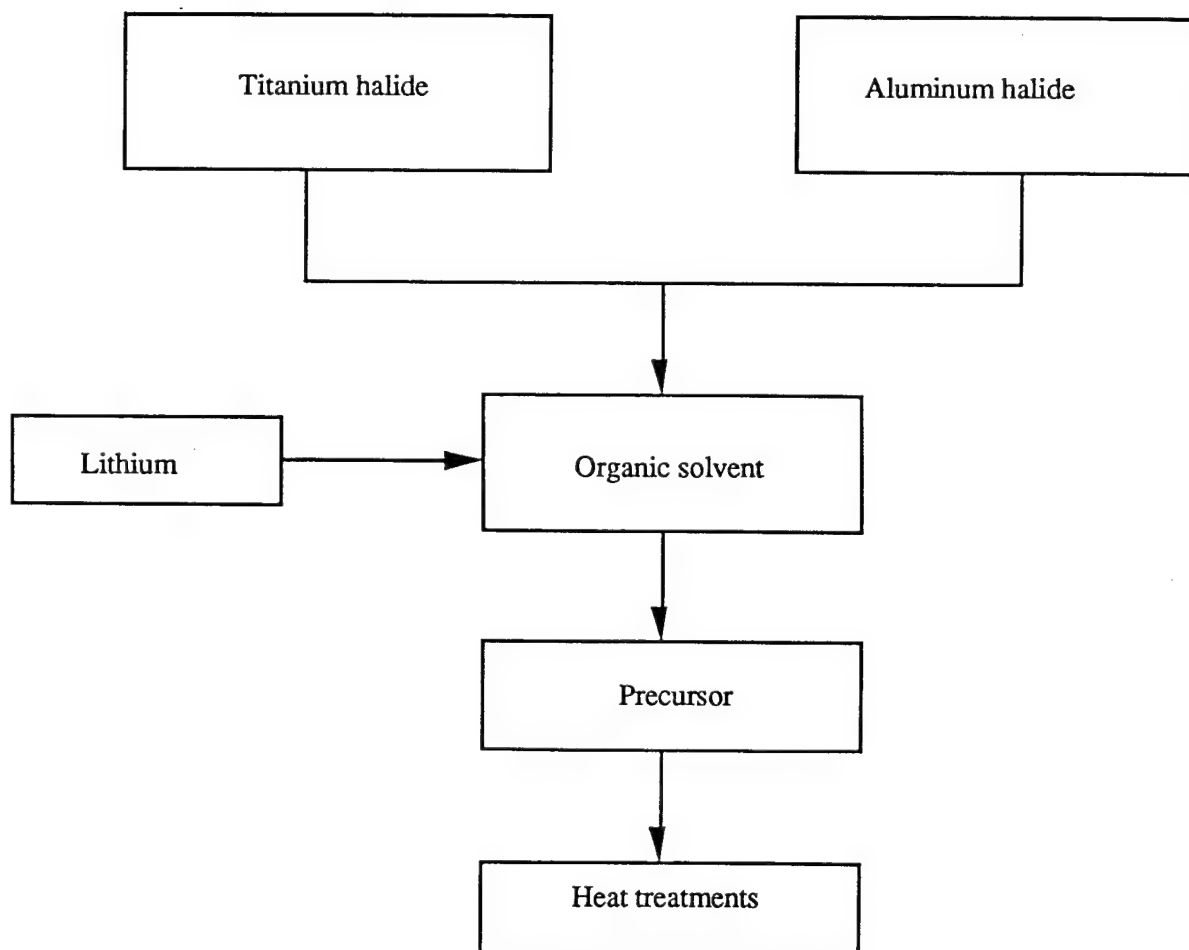
# Process I
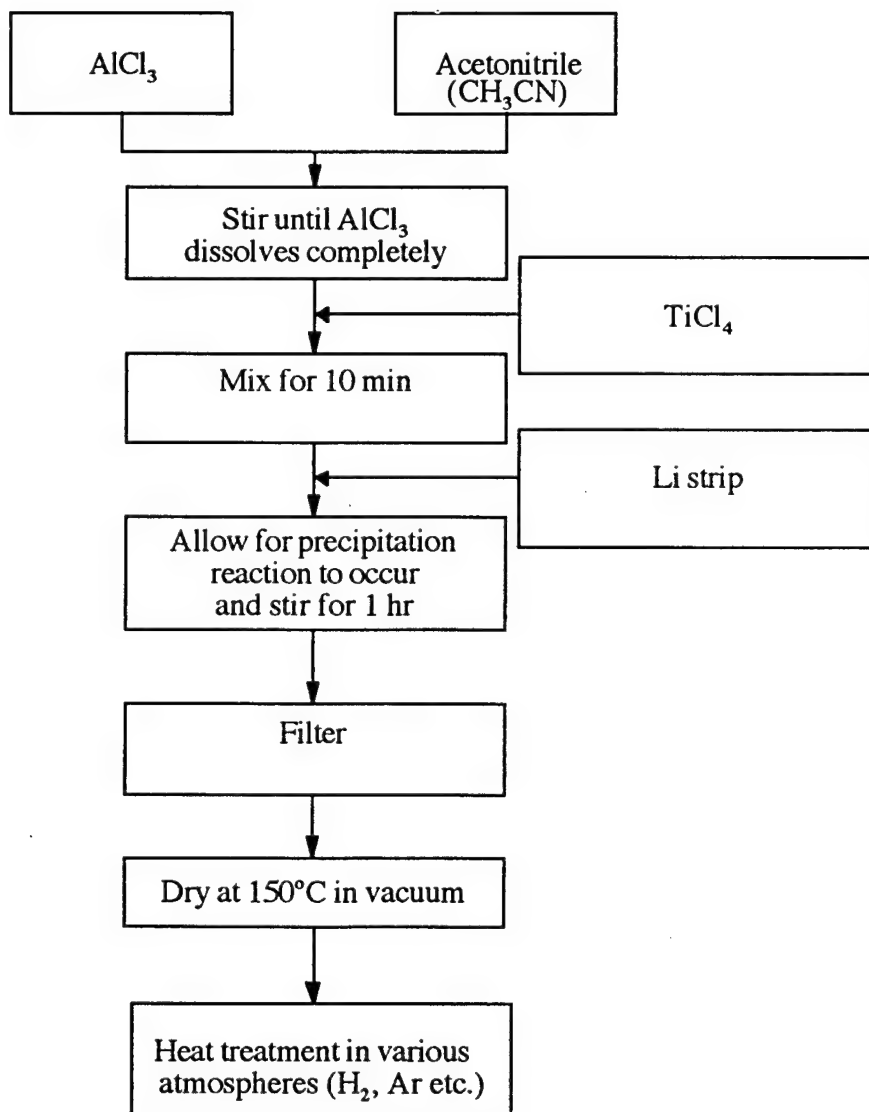


Figure 2. Flow sheet showing the procedure for synthesizing Titanium Aluminide using $TiCl_4$, $AlCl_3$ and Li metal strip in acetonitrile.
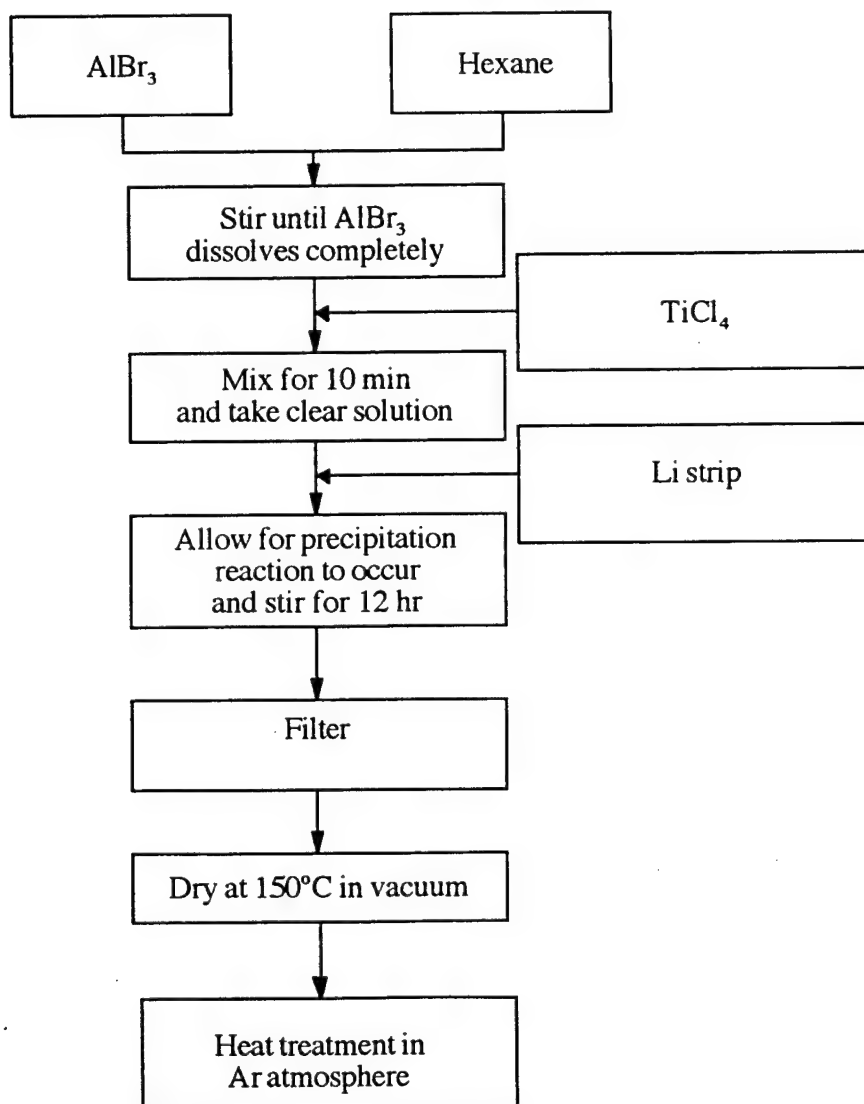
# Process II
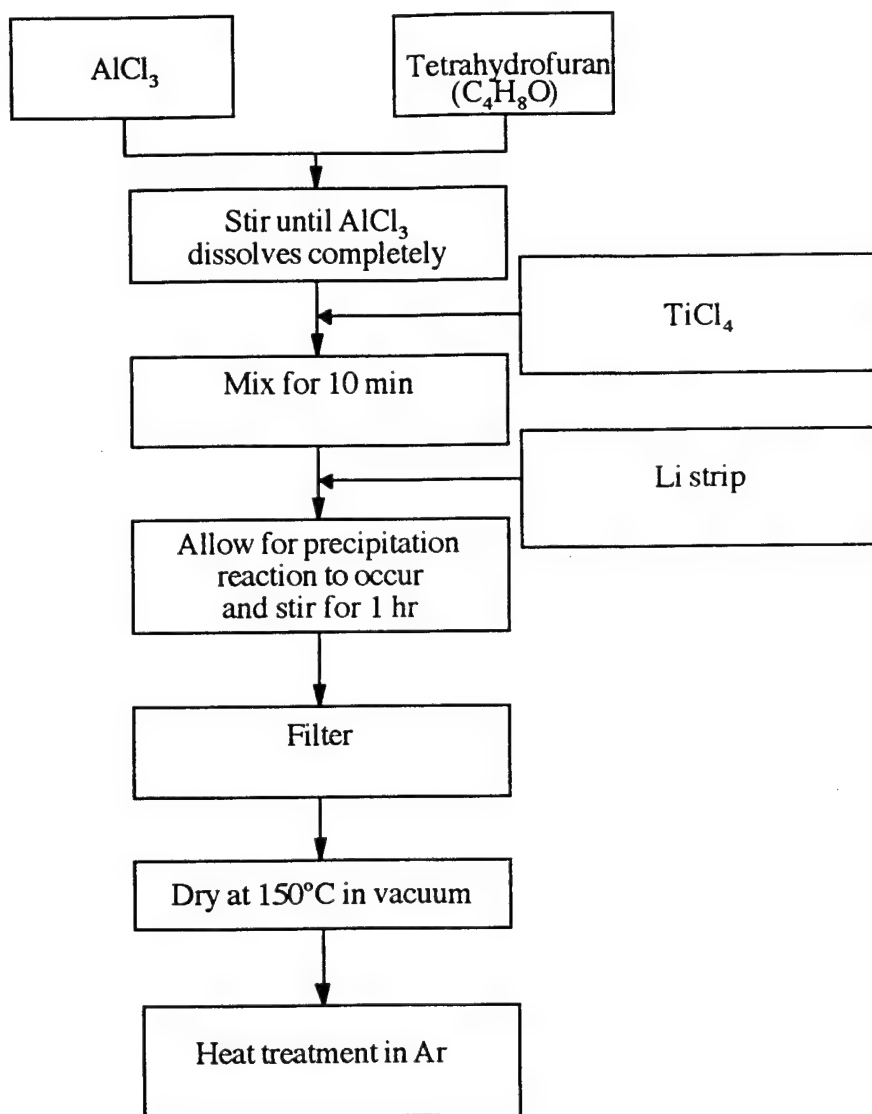


Figure 3.  Flow sheet showing the procedure for synthesizing Titanium Aluminide using $TiCl_4$, $AlCl_3$ and Li metal strip in THF.
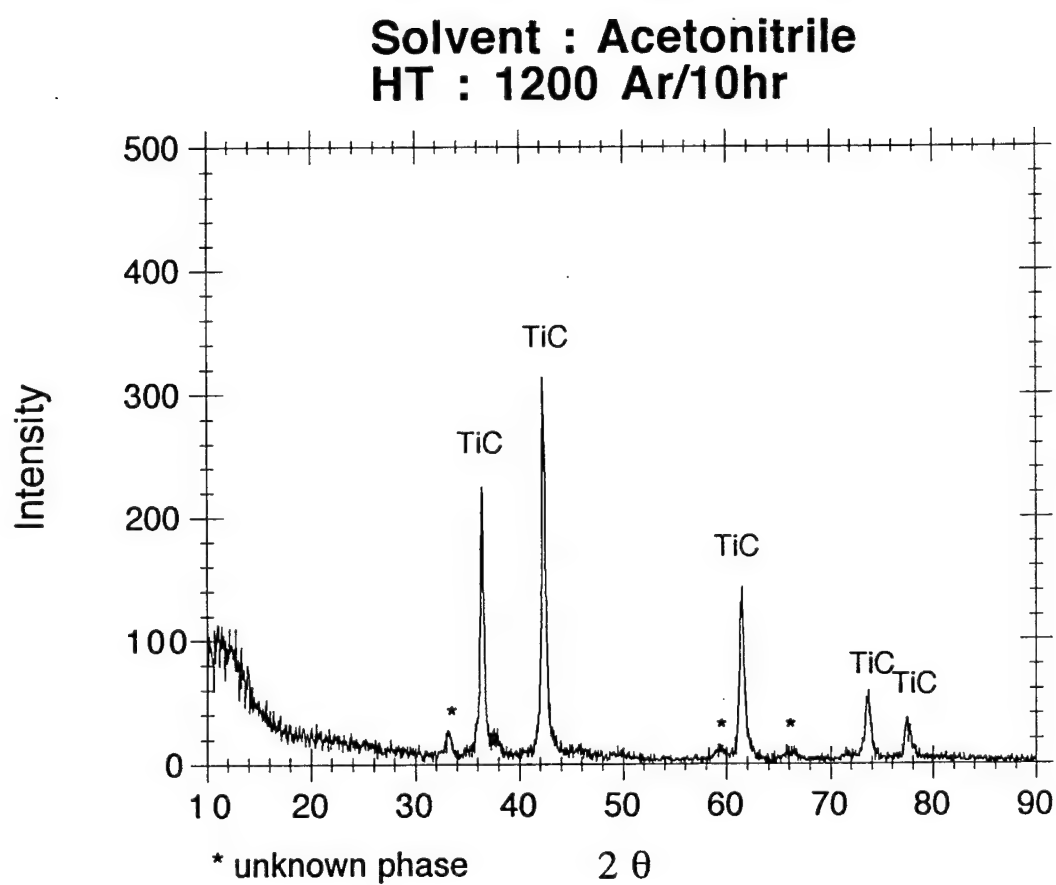
# Process III
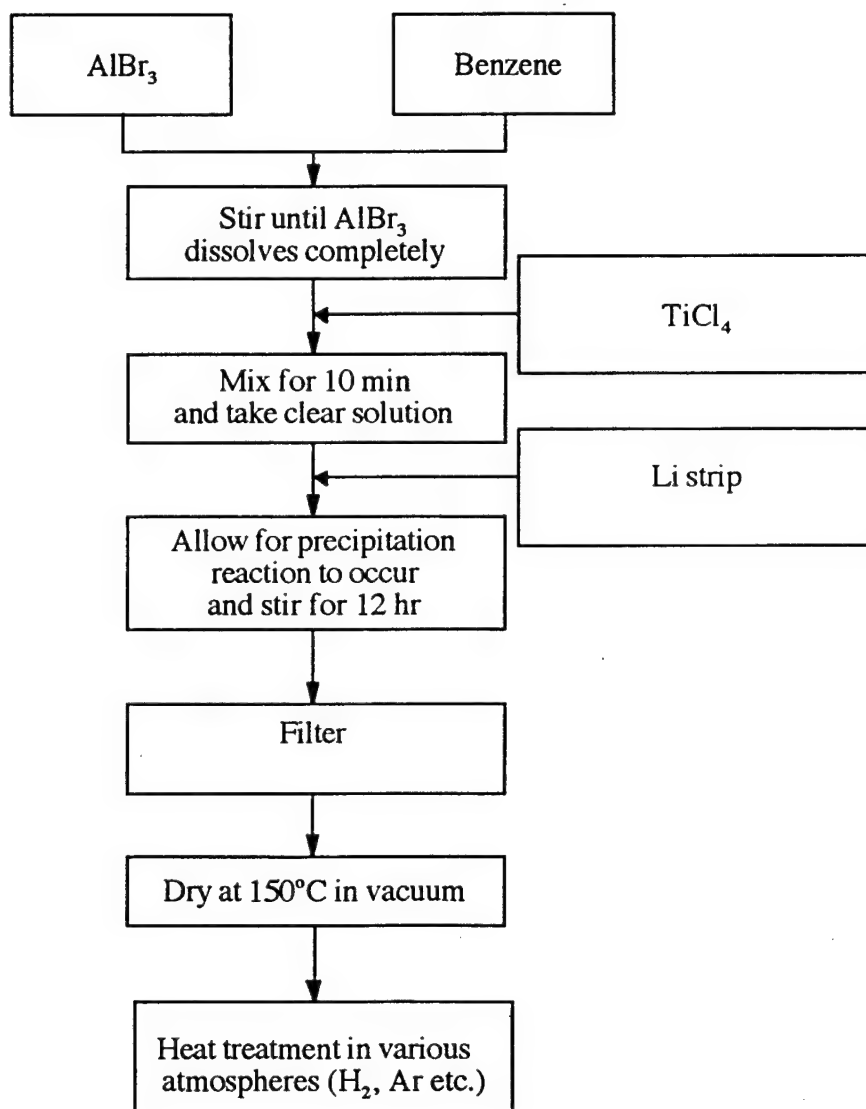


Figure 4. Flow sheet showing the procedure for Synthesizing Titanium Aluminide using $TiCl_4$, $AlBr_3$ and Li metal strip in Benzene.

# Process IV



Figure 5.  Flow sheet showing the procedure for Synthesizing Titanium Aluminide using $TiCl_4$, $AlBr_3$ and Li metal strip in Hexane.

Figure 6. X-ray diffraction pattern of powder obtained after heat treatment of precursor derived from Process I in Ar atmosphere.
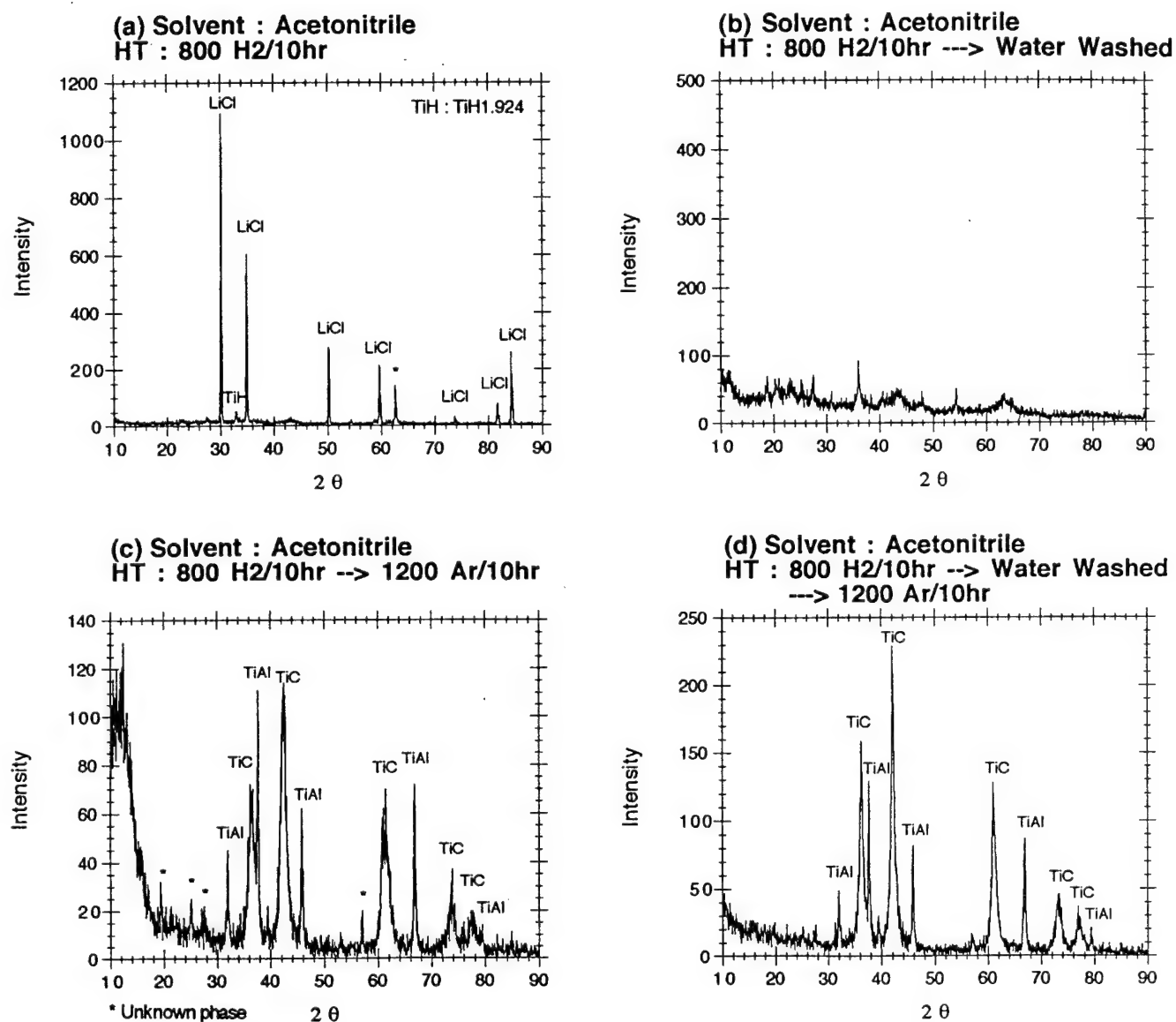
Figure 7. X-ray diffraction patterns of powders obtained after heat treatments of precursors derived from Process I in different atmospheres of $H_2$ and Ar.
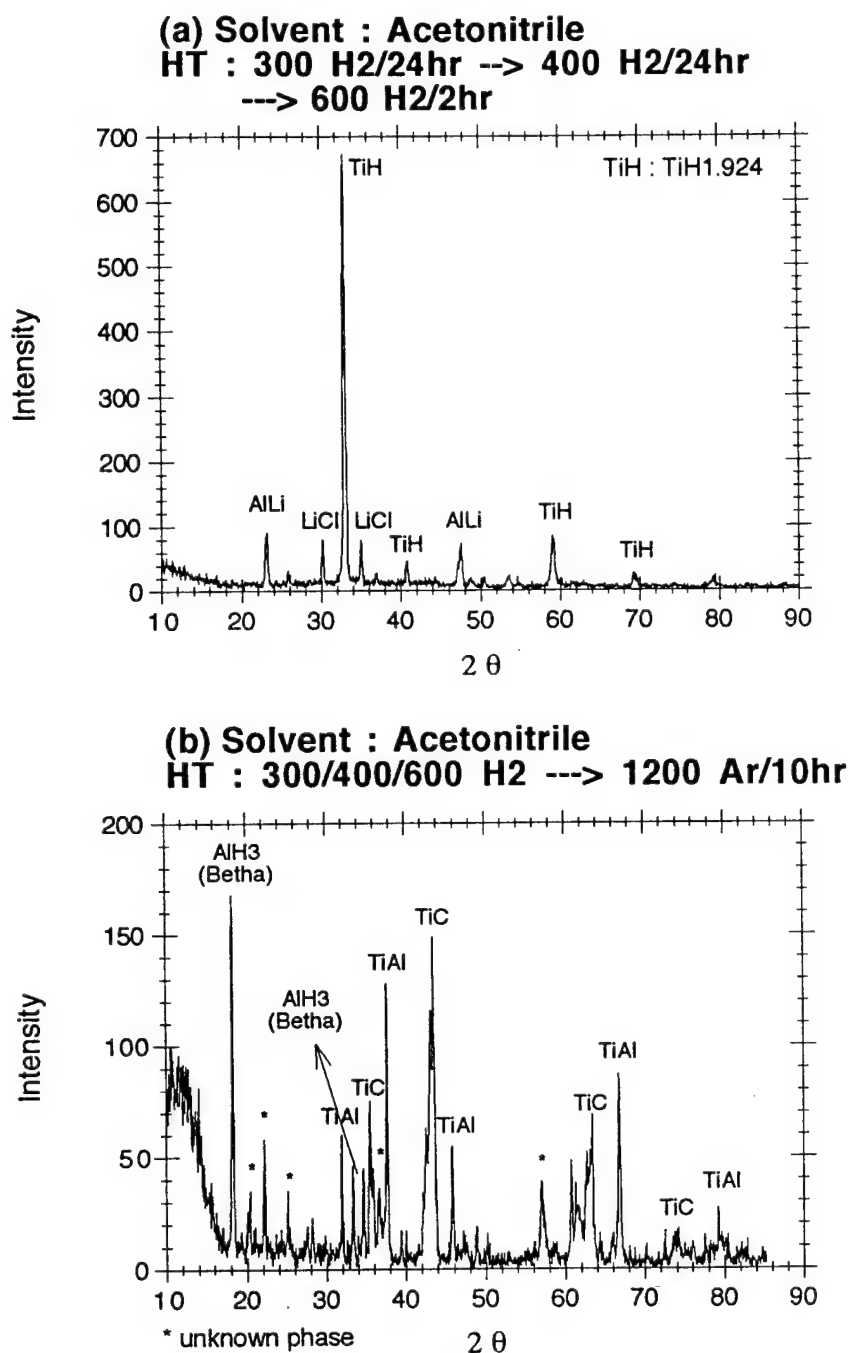
Figure 8. X-ray diffraction patterns of powders obtained after heat treatments of precursors derived from Process I. The patterns show the effect of low temperature $H_2$ pretreatment.

Figure 9. SEM micrograph showing the morphology of powders corresponding to those exhibiting X-ray pattern shown in Fig. 7(c). The powders were obtained after heat treatment of precursors derived from Process I.
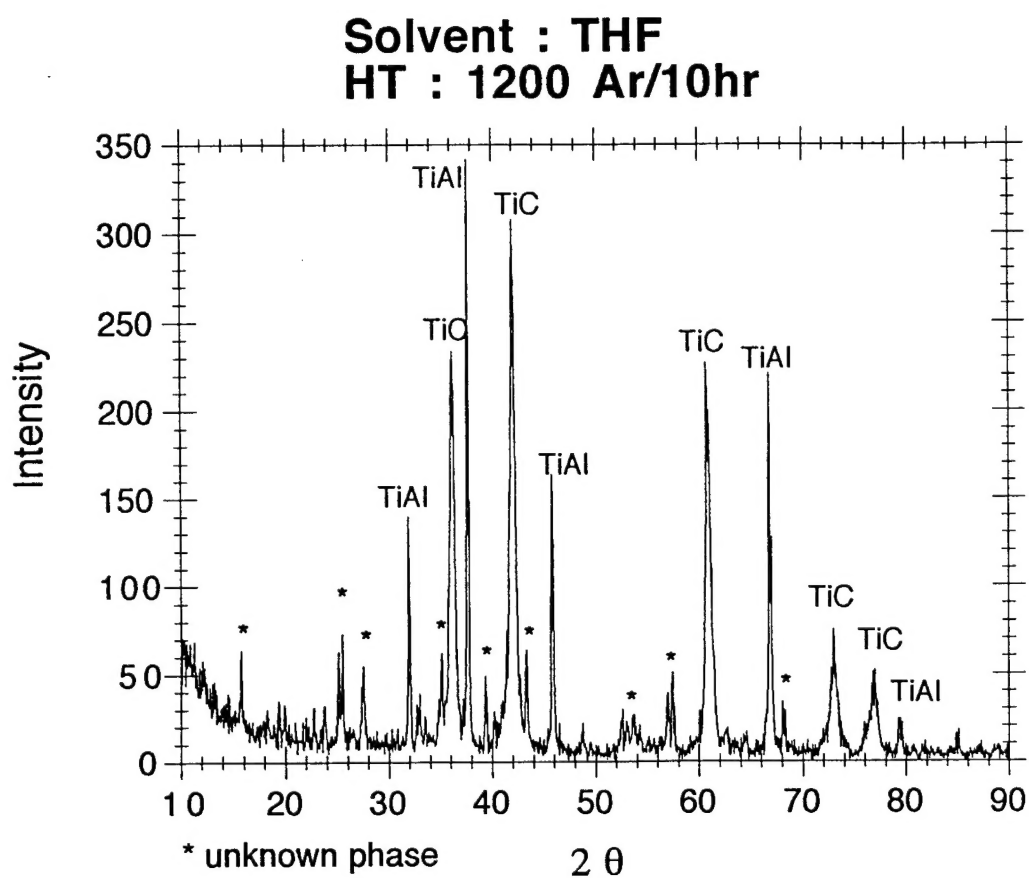
Figure 10. X-ray diffraction pattern of powder obtained after heat treatment of precursor derived from Process II. The patterns shows $\gamma$-TiAl, TiC and unknown phases as marked.
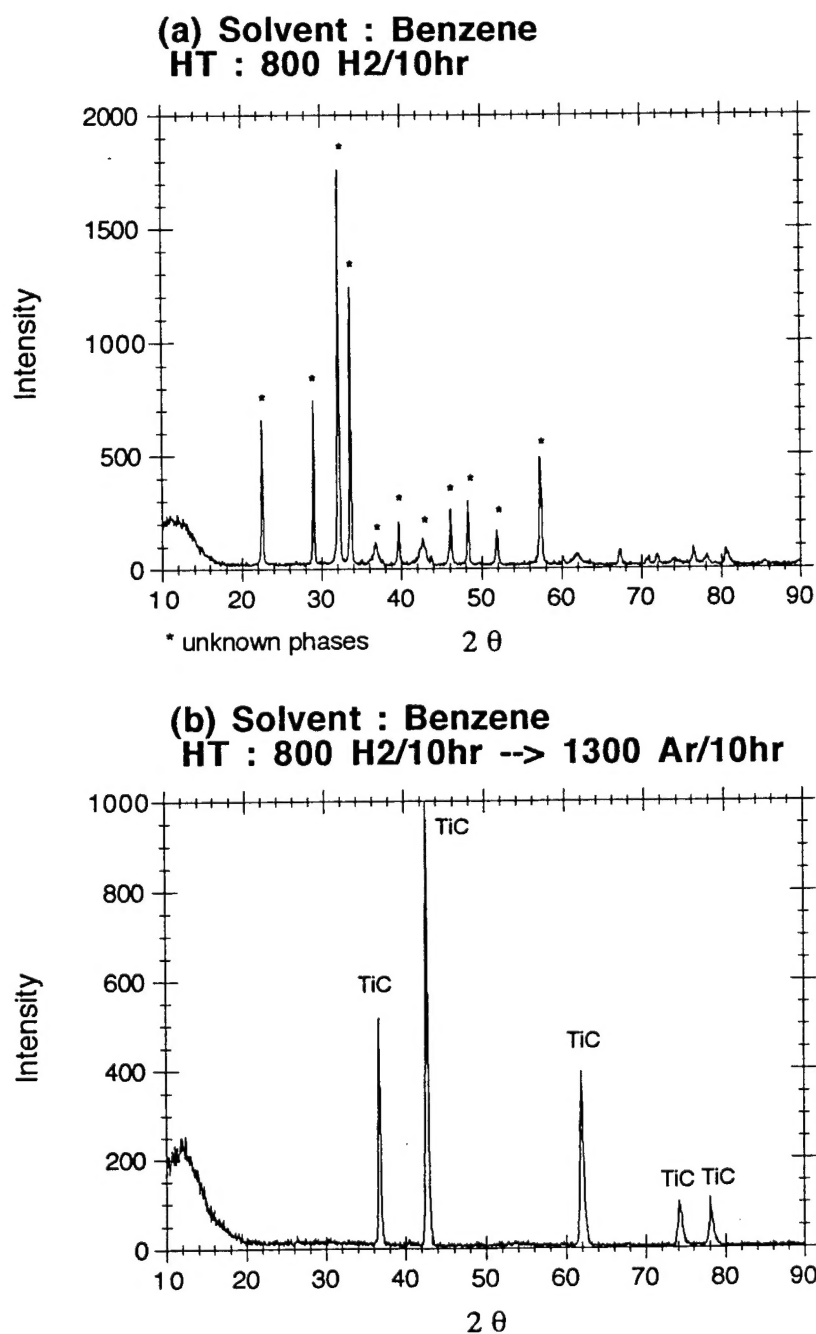
## (a) Solvent : Benzene
## HT : 800 H2/10hr



* unknown phases

## (b) Solvent : Benzene
## HT : 800 H2/10hr --> 1300 Ar/10hr



Figure 11. X-ray diffraction patterns of powders obtained after heat treatments of precursors derived from Process III in $H_2$ and Ar. Fig. 11(a) shows the presence of unknown phases while Fig. 11(b) shows clearly the presence of crystalline TiC.
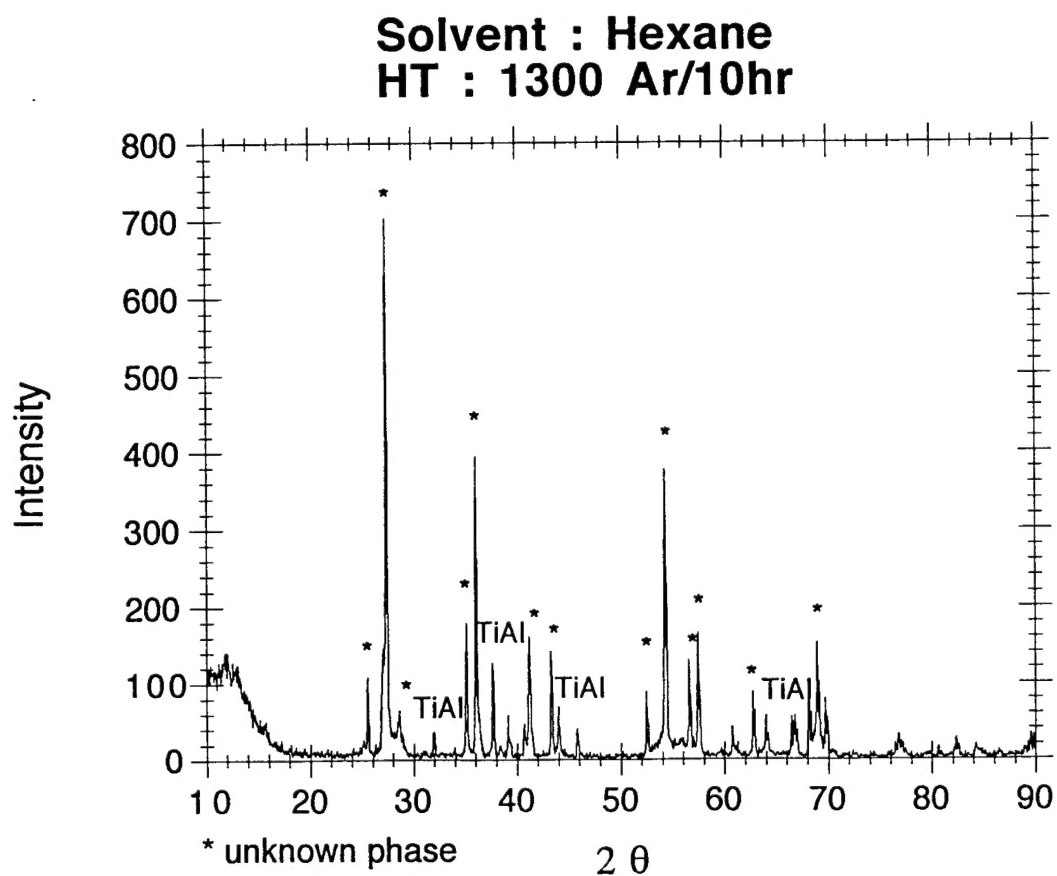
Figure 12. X-ray diffraction pattern of powder obtained after heat treatment of precursors derived from Process IV in Ar. The pattern shows the presence of γ-TiAl, TiC and unknown phases as marked.